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(54) Process for the non-catalytic production of hydrogen and/or carbon monoxide

(57) A process for the non-catalytic production from hydrocarbon-containing gases of gases essentially comprising hydrogen and/or carbon monoxide comprises: (i) an endothermic methane cracking step, essentially in the absence of steam, optionally followed by an endothermic watergas reaction step in the presence of steam, or (ii) an endothermic steam methane reforming step. The said hydrocarbon-containing gases are contacted with a heated mass of solids. The hydrogen and/or carbon monoxide-containing gas produced, after leaving the said mass of solids at a temperature of 900–1500°C, is quenched with a gas and/or steam and/or water to a temperature of 700–900°C.

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PROCESS FOR THE NON-CATALYTIC PRODUCTION OF A HYDROGEN-CONTAINING GAS

The invention relates to a process for producing non-catalytically a hydrogen-containing gas. In particular, the present invention relates to the non-catalytic production of hydrogen-containing gases from hydrocarbon-containing gases such as natural gas, associated gas (i.e. gas which is produced together with oil in production fields) and (waste) hydrocarbon gases from e.g. a Fischer-Tropsch synthesis, etc.

Many processes are already known for the conversion of hydrocarbonaceous material into hydrogen-containing gaseous products such as synthesis gas (which comprises in addition to hydrogen a substantial amount of carbon monoxide and usually small amounts of carbon dioxide, steam and/or unconverted hydrocarbons).

It is in particular known that hydrogen-containing gas can be produced from hydrocarbon-containing gases, by carrying out a process with alternating combinations of exothermic and endothermic reactions in a regenerator-type reactor, in which a heated mass of solids is used to provide heat required for carrying out endothermic cracking, watergas and steam methane reforming steps.

In such processes the following reactions are accomplished:

(i) the endothermic methane cracking reaction:

$$CH_4 \longrightarrow C + 2H_2 ,$$

(ii) the endothermic watergas reaction:

$$C + H_2O \longrightarrow CO + H_2$$

(iii) the endothermic steam methane reforming reaction:

$$CH_4 + H_2O \longrightarrow 3H_2 + CO$$

resulting in the production of synthesis gas or hydrogen. A problem is that the hot product gases upon cooling will give the reverse reactions which is of course disadvantageous.

It is therefore an object of the present invention to provide

a process for the non-catalytic production from hydrocarbon-containing gases of gases essentially comprising hydrogen and/or carbon monoxide wherein such a reverse reaction is avoided.

The invention therefore provides a process for the non-catalytic production from hydrocarbon-containing gases of gases essentially comprising hydrogen and/or carbon monoxide, by alternating combinations of exothermic and endothermic reactions in a regenerator-type reaction stove, said process comprising: (i) an endothermic methane cracking step, essentially in the absence of steam, optionally followed by (ii) an endothermic watergas reaction step in the presence of steam, or (iii) an endothermic steam methane reforming step, by contacting the said hydrocarbon-containing gases with a heated mass of solids, characterized in that the hydrogen and/or carbon monoxide-containing gas produced in steps (i), (ii), or (iii), after leaving the said mass of solids at a temperature of 900-1500 °C is quenched with a gas and/or steam and/or water to a temperature of 700-900 °C.

Advantageously a relatively hot quench gas can be used wherein the highest energy is extracted from the gas.

Hydrogen-containing gas is defined for the present purpose as substantially pure hydrogen or synthesis gas wherein the hydrogen/carbon monoxide molar ratio may vary.

The process according to the invention is suitably carried out in one or more fixed beds comprising a heated mass of solids. Fixed beds could be applied which may contain heat-resistant solid material in any desired shape and size, such as a fixed brick matrix or a packed bed of particulate solids. Particulate solids such as packed spheres or cylinders with main dimensions (e.g. diameter, height of the cylinder) of 1-50 mm, and in particular 2-50 mm, are suitably used in the present process.

Various solid materials may be used in the process according to the present invention provided that the material is sufficiently heat-resistant and can withstand large temperature variations which occur during start-up and shut-down of the process. Suitable solids

comprise refractory oxides, silicium carbide, carbonaceous materials (e.g. petrol cokes) and mixtures thereof. Metal alloys or metal compounds may also be suitably used; these materials have the advantage of possessing a relatively high thermal conductivity and volumetric heat capacity compared with the previously mentioned materials. Substantially non-catalytic solids will be most suited for use in the process according to the invention because the deposition of carbon on the surface of the solids will usually lead to a substantial decrease in catalytic activity, if present in fresh solids. Advantageously, the bed of solids comprises alumina beads and/or silica.

Both step (i) (cracking), step (ii) (watergas reaction) and step (iii) (steam methane reforming) are suitably carried out at a substantially equal pressure from 0.5-50 bar abs. and preferably from 5-20 bar abs.

Preheating of the solids applied in the process according to the invention to any temperature suitable for the purpose may be carried out in various ways. Advantageously, the solids are preheated to a temperature of 1400-1650 °C before being contacted with the hydrocarbon-containing gas. Suitably the solids are heated by combustion, preferentially under pressure of a fuel gas with an oxygen-containing gas and contacting the combustion gas with the solids, whereafter the combustion gas is cooled e.g. by preheating the hydrocarbon-containing gas and/or oxygen.

Various gaseous hydrocarbonaceous materials can be used as feed for the process according to the invention. In particular natural gas, methane, associated gas, LPG and evaporated naphtha are used. In some cases natural gas is preferably subjected to a treatment to remove sulphur and/or inorganic substances before using it as feed for the present process.

The invention also relates to hydrogen- or CO-containing gas obtained by a process as described hereinbefore.

The invention will now be described by way of example in more detail by reference to the following Examples.

EXAMPLE A

Hot product gas (98% H_2, 2% N_2) is obtained by thermal cracking of natural gas, in a blast furnace-type or regenerator-type reaction stove and leaving the stove at an average temperature of 1100-1400 °C is quenched with relatively cold product gas of 250-350 °C to a temperature of 700-900 °C, wherein said cold product gas after having been cooled down in any suitable heat exchanging device, is recycled via any suitable line to the hot product gas leaving the stove. For each ton of hot gas 1.05 ton of quench gas is required.

Of the potential useful sensible heat in the hot gas leaving the stove nothing is lost and all can be used for raising steam which can be applied in the process. Blast furnace-type or regenerator-type stoves as such are known to those skilled in the art and will not be described in detail.

In this case a recycle gas compressor is applied.

EXAMPLE B

Hot product gas (72% H_2, 24% CO, 1 CO_2, 2% N_2, 1% H_2O) is obtained by thermal Steam Methane Reforming of natural gas, in a blast furnace-type or regenerator-type reaction stove and leaving the stove at an average temperature of 1100-1400 °C is quenched with steam of 200-500 °C to a temperature of 700-900 °C. For each ton of hot syngas leaving the stove at 1350 °C 2.5 ton of steam of 400 °C are required to quench the gas to 900 °C.

In this case not all the potential sensible heat in the hot gas leaving the stove is available for steam raising as the heat required for raising the quench steam has generally to be subtracted. However the quench steam will generally be Low Pressure steam imported from e.g. a downstream synthesis process (methanol) and in that case this loss can be neglected. An advantage of quenching with steam or water is that no recycle gas compressor is required.

EXAMPLE C

It is also possible to quench the hot product gas (the same as used in Example A) with water of 30-120 °C. In that case for each

ton of hydrogen of 1100-1400 °C, 2.1 tons of water of 30-120 °C are required to quench the hot product gas to 700-900 °C.

Various modifications of the present invention will become apparent to those skilled in the art from the foregoing description. Such modifications are intended to fall within the scope of the appended claims.

CLAIMS

1. A process for the non-catalytic production from hydrocarbon-containing gases of gases essentially comprising hydrogen and/or carbon monoxide by alternating combinations of exothermic and endothermic reactions in a regenerator-type reaction stove, said process comprising: (i) an endothermic methane cracking step, essentially in the absence of steam optionally followed by (ii) an endothermic watergas reaction step in the presence of steam, or (iii) an endothermic steam methane reforming step, by contacting the said hydrocarbon-containing gases with a heated mass of solids, characterized in that the hydrogen and/or carbon monoxide-containing gas produced in steps (i), (ii), or (iii) after leaving the said mass of solids at a temperature of 900-1500 °C is quenched with a gas and/or steam and/or water to a temperature of 700-900 °C.

2. The process as claimed in claim 1, characterized in that the gas produced is quenched with relatively cold recycle gas.

3. The process as claimed in claim 2, characterized in that the gas produced leaves the mass of solids at a temperature of 1100-1400 °C and is quenched with relatively cold recycled product gas of 250-350 °C to a temperature of 700-900 °C.

4. The process as claimed in claim 1, characterized in that the gas produced is quenched with water.

5. The process as claimed in claim 4, characterized in that the gas produced is quenched with water of 30-120 °C to a temperature of 700-900 °C.

6. The process as claimed in claim 1, characterized in that the gas produced is quenched with steam.

7. The process as claimed in claim 6, characterized in that the gas produced leaves the mass of solids at a temperature of 1100-1400 °C and is quenched with steam of 200-500 °C to a temperature of 700-900 °C.

8. The process as claimed in any one of claims 1-7, characterized in that the hydrocarbon-containing gas is natural gas.

9. Hydrogen-containing gas whenever obtained by the process as claimed in any one of claims 1-8.

10. CO-containing gas whenever obtained by the process as claimed in any one of claims 1-8.

Patents Act 1977
Examiner's report to the Comptroller under Section 17 (The Search Report)

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Relevant Technical fields

(i) UK Cl (Edition L) C5E (EAS EAT)

(ii) Int Cl (Edition 5) C01B

Databases (see over)

(i) UK Patent Office

(ii)

Search Examiner

R J WALKER

Date of Search

12 MAY 1993

Documents considered relevant following a search in respect of claims 1-10

Category (see over)	Identity of document and relevant passages		Relevant to claim(s)
X	GB 2235464 A	(EXXON RESEARCH AND ENGINEERING CO) see page 3 line 21 - page 5 line 2 and page 7 lines 1-13	at least 1, 4, 8, 9, 10
X	GB 1025192 A	(PULLMAN INC) see page 5 lines 13-34	at least 1, 4, 6, 8, 9, 10
A	EP 0219163 A	(SHELL INTERNATIONALE RESEARCH) see whole document	at least 1

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

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